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Optimization Studies on Catalytic Pyrolysis of Empty Fruit Bunch (EFB) Using L9 Taguchi Orthogonal Array

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In this investigation, catalytic pyrolysis of empty fruit bunch (EFB) was studied and optimized in terms of bio-oil and char yields by using Taguchi L9 Orthogonal Array method. The effects of pyrolysis temperatures, catalyst loadings and particle sizes on the product yields were investigated and discussed in this paper. The catalytic pyrolysis is performed in a semi-batch reactor which is externally heated by an electrical vertical split tube furnace. Under the nitrogen flow rates of 60 ml/min, 80 mL/min and 100 mL/min, 15 g of EFB biomass with the particle sizes of 100 µm, 250 µm, 500 µm were thermally decomposed at three pyrolysis temperatures of 573 K, 673 K and 773 K, along with Zeolite HZSM-5 catalyst loadings of 1 wt%, 5 wt% and 12 wt%. From the product analysis, a maximum liquid bio-oil yield of 64.4 wt% were obtained at catalyst loading of 1.5 wt.%, reaction temperature of 773 K, nitrogen flow rate of 100 mL/min, and particle size of 250 µm. Meanwhile, at catalyst loading of 3.25 wt.%, reaction temperature of 773 K, nitrogen flow rate of 60 mL/min and particle size of 250 µm, the bio char yield formed was as low as 18.6 wt.% which could be mainly attributed to secondary cracking of char residue.

1. Introduction

With the escalating global tensions associated with fossil fuel shortage and environmental consequences of an ever increasing consumption of non-renewable resources, many research programs are devoted in developing new renewable energy resources with the hope in replacing the depleting crude fuel energy. Biomass has been discovered as the most attractive renewable energy source in comparison to wind and solar because biomass can be converted into liquid, solid and gaseous fuels and a range of speciality chemicals (Choi et al., 2014). With the proper catalyst and biomass feedstock, liquid fuel with high calorific value and good hydrocarbon distribution can be thermally produced from catalytic cracking of carbon-carbon bonds and de-oxygenation reaction in pyrolysis process.
Pyrolysis has been widely recognized as one of the most promising technologies for liquid bio-oil production along with the co-formation of solid char and gaseous products. Bio oil is a complex liquid mixture of water, ketones, sugars, furans, phenols, aldehydes, and guaiacols. Typically, it has to be further processed into liquid transportation fuels and value-added products, such as food flavorings, resins, fertilizer and fine chemicals, through cracking process. (Bridgwater and Peacocke, 1999).
In recent years, much pyrolysis works have been focused on using various types of biomass resources such as corn stalk, food waste, pine wood biomass and others (Zhang et al., 2015). In the present study, Empty Fruit Brunch (EFB) is incorporated as the biomass feedstock due to its vast availability and quantity. In Malaysia, a total of 18 million fibrous fibres were produced as biomass waste throughout Malaysia in the year of 2010 and expected more for subsequence years (Abdullah and Gerhauser, 2008). Thus, an attempt on using EFB as the feedstock in thermal pyrolysis process is carried out with the hope of improving the yield of bio-oil produced from conventional biomass resources. To improve and optimize the bio-oil production, Taguchi's Orthogonal Array method, a robust statistical and mathematical technique widely employed in many engineering applications, especially in manufacturing sector is incorporated into the present investigation. It is capable of studying multiple quality characteristic aspects and determining

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the most significant parameters of the processes. Unlike Response Surface Methodology (RSM), the orthogonal array method allows easier analysis with minimum number of experimental runs and the analysis result is valid over the entire region spanned by the control factors and its respective settings.

2. Materials and methods

2.1 Feedstock Preparation and Characterization

Empty Fruit Bunch (EFB) was obtained from FELCRA Berhad Nasaruddin, Bota, Perak, Malaysia. The particle size of the EFB is reduced with a Cutting Mill and is sieved to a particle size of 100 µm, 250 µm, 500 µm. At 110 °C the samples are dried in an oven for more than 24 h. The proximate analysis of the bulk EFP is conducted using Thermogravimetry EXSTAR TG/DTA 6300 and ultimate analysis is carried out using LECO 932 CHNS Analyzer.

Table 1: Characteristics of Empty Fruit Bunch (EFB)

Proximate Analysis (wt%)		Ultimate Analysis (wt%)	
Moisture	5.3	Carbon, C	45.01
Volatile Matter	71.00	Hydrogen, H	4.88
Fixed Carbon	16.80	Oxygen, O	49.02
Ash	6.90	Nitrogen, N	0.78
High Heating Value, HHV (MJ/Kg)	20.20	Sulphur, S	0.31

2.2 Catalyst Preparation and Characterization

The zeolite HZSM-5 employed in this experimental work was obtained from Zeolyst International with the SiO_2/Al_2O_3 mole ratio of 30 and surface area of 400 m^2/g. Brunauer–Emmett–Teller (BET) specific surface area and mircropore volume of the catalyst samples were determined by using Surface Area Analyser Micromeritics ASAP 2021. For the preparation, the catalysts materials were calcined under nitrogen flow at a temperature of 773 K for 5 h in tube furnace reactor.

2.3 Experimental Setup

Prior the experiment starts, the initial weight of empty borosilicate tube, glass wool, catalyst, condenser and rubber tube are weighed and recorded. 15 g of EFP biomass is introduced into the borosilicate tube before the glass wool and catalysts are filled in. The zeolite catalyst is weighed accordingly as indicated in the Table 2. With nitrogen gas flow of 500 mL/min, the tube is tighten and purged for 5 min in order to drive out all of the oxygen or residue air contents present in the tube. After 5 min of degassing, the nitrogen flow and the temperature are set at the desired flow rate and reaction temperature respectively with the flow controllers. For the heating rate, the furnace is kept heating up at 20 °C/min. After heating up the pyrolyser unit, the liquefied product is collected in the condenser unit at which the mixture of vapour and nitrogen carrier gas is passed through the ice bath before condensing. After completion of each run, the reactor is left to cool down to room temperature before analysis of product is conducted. After the experiment, the condenser, rubber tube, borosillicate tube with glass wool and the catalyst are weighed individually.

Table 2: Experimental runs and corresponding parameters determined from L9 Taguchi Orthogonal Array

Run	Catalysis Loading (wt%)	Temperature (K)	Nitrogen Flow Rate (mL/min)	Particle Size (µm)
1	3.25	573	80	500
2	3.25	673	100	100
3	5	573	100	250
4	1.5	573	60	100
5	5	673	60	500
6	1.5	673	80	250
7	5	773	80	100
8	1.5	773	100	500
9	3.25	773	60	250

2.4 Bio-oil and Bio-char Yields Analysis

For the product analysis, the weight of bio-oil formed is computed by the weight difference of the weight of the condenser before and after each complete run. To calculate the weight of bio-char produced, the total weight of the glass tube after reaction is deducted with the total weight of the glass tube, catalyst and glasswool before the reaction. With reference to Rahman et al (2014), the percentage of char and liquid product yields were defined as Eq(1).

$$\frac{Weight\ of\ solid\ char\ or\ bio\ oil\ (g)}{Weight\ of\ dried\ OPF\ used\ \ (g)}\ X\ 100\% \tag{1}$$

In the context of experimental optimization, Design Expert 8.0.6.1 software, a statistical software which incorporates Taguchi's L9 Orthogonal Array method is used in order to determine the optimized operating conditions. A total of 9 significant experimental runs is determined from the statistical software instead of 81 runs as the present study involves 4 reaction parameters (Catalyst Loadings, Temperature, Nitrogen Flow and Particles Size) and 3 levels each. These 9 experiment runs helped in the systematic approach for data analysis and identification of parameters that affect the oil production. Using the Design Expert software, the relationship between the variables is established and analysis is conducted for each parameter. The experiment is repeated at different operating conditions based on Taguchi L9 Orthogonal Array as shown in Table 2. To determine the effects of each variable on the product yields, a variance index, Signal-to-Noise (S/N) ratio is calculated by using the equations as shown as Eq (2) and (3). Among the three quality characteristics, "the bigger the better" is used as the determining factor to define and verify the liquid product yields, whereas "the smaller the better" is used to verify the solid product yields since the higher liquid yield and lower solid yield is desirable from the pyrolysis process.
For maximizing the liquid product yield, the following definition of S/N ratio can be calculated as below:

$$\frac{S}{N} = -10\log\left(\frac{1}{r}\sum_{i=1}^{r}\frac{1}{y_i^2}\right) \tag{2}$$

For minimizing the solid yield, the following definition of S/N ratio can be calculated as below:

$$\frac{S}{N} = -10\log\left(\sum_{i=1}^{r}\frac{y_i^2}{r}\right) \tag{3}$$

Where r is the number of tests in trial, y_i is the experimental response at i^{th} repetition. In order to evaluate the significance of each individual factor on product yields, the average S/N ratio for each factor f at level j is computed for each factor level as shown in Eq (4):

$$\frac{S}{N} = \frac{Sum\ of\ S/N\ \ values\ for\ factor\ i\ at\ level\ j}{3} \tag{4}$$

3. Results and discussion

3.1 Optimum Conditions by Taguchi L9 Orthogonal Array

From Table 5, the maximum bio-oil yield was found at catalyst loading of 1.5 wt.%, temperature of 773 K, nitrogen flow rate of 100 mL/min and particle size of 250 µm with the yield as high as 64.43 wt.%. On another hand, it was also found that the lowest char residue was 18.6 wt% which occurred at catalyst loading of 1.5 wt.%, temperature of 773 K, nitrogen flow rate of 60 mL/min and particle size of 250 µm. As can be seen from Table 3, the range of S/N ratio is the highest referring to particle size, followed by pyrolysis temperature, then nitrogen flow rate and catalyst loadings. Such ranking indicates that the particle size has a more pronounced effect on the liquid product yield and a small change in the particle size causes a larger influence on the liquid yield, resulting in larger S/N ratio range. Whereas, from Table 4, the factors affecting the solid yield have the opposite ranking as to that affecting the liquid product yields. This is in good agreement with the fact that the higher the liquid yields, the lower the solid yields.

3.2 Effect of Catalyst Loading and Particle Size on Bio-Oil and Residue Char Yields

Based on the analysis result, pyrolysis of EFB produces the highest yield of bio-oil at intermediate catalyst loading of 1.5 wt.% and lowest yield of bio-char at catalyst loading of 3.25 wt.%. Such results are consistent with the work reported by Ahoa, et al. (2008) as increasing catalyst loadings lead to more biomass decomposition toward gas products due to the presence of strong bronsted acid sites on the H ZSM-5 surface. In the context of solid yield, the char yields decreases proportionally with higher catalyst loadings as the maximum char yield occurs at catalyst loading of 1.5 wt.% and the minimum char yield occurs at 3.25 wt.%. When the amount of catalysts loaded increases, more volatile matters are being catalyzed and reacted which contributed to a higher liquid product yield and consequently, a lower char yield.

For the pyrolysis of EFB with particle size of 250 µm, it yielded a maximum liquid product of 35 wt.% before it dropped back to less than 20 wt.% at particle size of 500 µm. Such trend could be elucidated as the small biomass particles is more favorable to overheating and experienced secondary polymerization reaction which in turns resulted in high gas yield (Kamaroddin et al., 2014). Large particle size of 500 µm experienced large temperature gradient within the particles, which possibly leads to partial biomass decomposition and gives rise to an increase in the solid yields. Similar trends are reported in the research works made by Azri et al. (2009).

3.3 Effect of Reaction Temperature and Nitrogen Flow Rate on Bio-oil and Residue Char Yields

For reaction temperature, the highest bio-oil yield and lowest char yield were obtained at the highest reaction temperature of 773 K which is in good agreement to that reported in Sulaiman (2011)'s work. At high temperature, more volatile matters are released from the biomass structure and decomposed before converted into the liquid product, which in turns resulted in the declining trend of char weight. The decrease in char yield could be due to primary decomposition of EFB at high temperature or by secondary decomposition of the char residue. In term of nitrogen flow rate, the maximum liquid bio-oil and bio-char was obtained at the highest flow rate of 100 mL.

Table 3: Average S/N ratio of bio-oil yields at each factor and level

Factors	Levels	S/N Average	Range	Rank
	1.5	32.4		
Catalysis Loading (wt%)	3.25	27.7	4.7	4
	5	31.6		
	300	26.9		
Temperature (℃)	400	31.8	6.2	2
	500	33.1		
	60	30.9		
Nitrogen Flow Rate (mL/min)	80	27.7	5.3	3
	100	33.1		
	100	20.9		
Particle Size (µm)	250	32.8	11.8	1
	500	27.2		

Table 4: Average S/N ratio of solid yields at each factor and level

Factors	Levels	S/N Average	Range	Rank
	1.5	-32.11		
Catalysis Loading (wt%)	3.25	-31.57	2.9	1
	5	-31.50		
	300	-29.10		
Temperature (°C)	400	-31.93	2.1	3
	500	-25.39		
	60	-30.76		
Nitrogen Flow Rate (mL/min)	80	-29.16	2.5	2
	100	-29.51		
	100	-32.10		
Particle Size (µm)	250	-31.57	1.9	4
	500	-31.50		

Table 5: Pyrolysis product yields based on Taguchi's L9 Orthogonal Array estimations

Run	Catalysis Loading (wt%)	Temperature (K)	Nitrogen Flow Rate (mL/min)	Particle Size (µm)	Oil Yield (%)	Char Yield (%)
1	1.5	573	60	100	32.40	40.30
2	1.5	673	60	100	44.13	41.23
3	1.5	773	60	100	50.03	34.57
4	3.25	573	60	100	21.17	30.57
5	3.25	673	60	100	32.90	31.50
6	3.25	773	60	100	38.80	24.83
7	5	573	60	100	28.10	32.73
8	5	673	60	100	39.83	33.67
9	5	773	60	100	45.73	27.00
10	1.5	573	80	100	28.37	43.20
11	1.5	673	80	100	40.10	44.13
12	1.5	773	80	100	46.00	37.47
13	3.25	573	80	100	17.13	33.47
14	3.25	673	80	100	28.87	34.40
15	3.25	773	80	100	34.77	27.73
16	5	573	80	100	24.07	35.63
17	5	673	80	100	35.80	36.57
18	5	773	80	100	41.70	29.90
19	1.5	573	100	100	42.30	48.30
20	1.5	673	100	100	54.03	49.23
21	1.5	773	100	100	59.93	42.57
22	3.25	573	100	100	31.07	38.57
23	3.25	673	100	100	42.80	39.50
24	3.25	773	100	100	48.70	32.83
25	5	573	100	100	38.00	40.73
26	5	673	100	100	49.73	41.67
27	5	773	100	100	55.63	35.00
28	1.5	573	60	250	36.90	34.07
29	1.5	673	60	250	48.60	35.00
30	1.5	773	60	250	54.50	28.33
31	3.25	573	60	250	25.67	24.33
32	3.25	673	60	250	37.40	25.27
33	3.25	773	60	250	43.30	18.60
34	5	573	60	250	32.60	26.50
35	5	673	60	250	44.30	27.43
36	5	773	60	250	50.23	20.77
37	1.5	573	60	500	23.07	35.33
38	1.5	673	60	500	34.80	36.27
39	1.5	773	60	500	40.70	29.60
40	3.25	573	60	500	11.83	25.60
41	3.25	673	60	500	23.57	26.53
42	3.25	773	60	500	29.47	19.87
43	5	573	60	500	18.77	27.77
44	5	673	60	500	30.50	28.70
45	5	773	60	500	36.40	22.03
46	1.5	573	80	250	32.87	36.97
47	1.5	673	80	250	44.60	37.90
48	1.5	773	80	250	50.50	31.23
49	3.25	573	80	250	21.63	27.23
50	3.25	673	80	250	33.37	28.17
51	3.25	773	80	250	39.27	21.50
52	5	573	80	250	28.57	29.40
53	5	673	80	250	40.30	30.30
54	5	773	80	250	46.20	23.67
55	1.5	573	80	500	19.03	38.23

Table 6: Pyrolysis product yields based on Taguchi's L9 Orthogonal Array estimations (Cont.)

Run	Catalysts Loading (wt%)	Temperature (K)	Nitrogen Flow Rate (ml/min)	Particles Size (µm)	Oil Yield (%)	Char Yield (%)
56	1.5	673	80	500	30.77	39.17
57	1.5	773	80	500	36.67	32.50
58	3.25	573	80	500	7.80	28.50
59	3.25	673	80	500	19.53	29.43
60	3.25	773	80	500	25.43	22.77
61	5	573	80	500	14.73	30.67
62	5	673	80	500	26.47	31.60
63	5	773	80	500	32.37	24.93
64	1.5	573	100	500	32.97	43.33
65	1.5	673	100	500	44.70	44.27
66	1.5	773	100	500	50.60	37.60
67	3.25	573	100	500	21.73	33.60
68	3.25	673	100	500	33.47	34.53
69	3.25	773	100	500	39.37	27.87
70	5	573	100	500	28.67	35.77
71	5	673	100	500	40.40	36.70
72	5	773	100	500	46.30	30.03
73	1.5	573	100	250	46.80	42.07
74	1.5	673	100	250	58.53	43.00
75	1.5	773	100	250	64.43	36.33
76	3.25	573	100	250	35.57	32.33
77	3.25	673	100	250	47.30	33.27
78	3.25	773	100	250	53.20	26.60
79	5	573	100	250	42.50	34.50
80	5	673	100	250	54.23	35.40
81	5	773	100	250	60.13	28.77

4. Conclusion

With the incorporation of Taguchi's Orthogonal Array Method, catalytic pyrolysis of palm oil waste biomass, Empty Fruit Bunch (EFB) was successfully optimized with the highest oil yield of 64.4 wt% and lowest char yield of 18.6 wt. The highest bio-oil yield was obtained at an optimum temperature of 773 K with the catalyst loading of 1.5 wt% and nitrogen flow rate of 100 mL/min as well as particle size of 250 µm. While, the lowest bio-oil char yield is achieved under temperature of 773 K, catalyst loadings of 1.5 wt%, nitrogen flow rate of 60ml/min and particle size of 250 µm. The most significant factor affecting the bio-oil yield is particle size, followed by pyrolysis temperature, then nitrogen flow rate and catalyst loadings.

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